Paraffins of Cigar Smoke

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Column chromatography was used to isolate a fraction from cigar smoke condensate containing a homologous series of normal paraffinic hydrocarbons; the individual hydrocarbons were separated by gas-liquid chromatography and characterized by their infrared spectra, mass spectra, and gas chromatographic behavior. Those compounds identified include the normal paraffins from dodecane to pentacosane. This fraction was isolated from the smoke condensates of four cigar types containing unblended filler tobacco that varied considerably in smoking characteristics. Qualitatively, the four types were identical, but quantitative differences were observed.

In an attempt to elucidate those factors that contribute to the aroma of cigars, we have been systematically investigating the chemical constituents of cigar smoke condensate. In previous publications (1, 2) we discussed the isolation and identification of volatile basic and phenolic constituents found therein. More recently we have investigated the hydrocarbon fraction of the condensate and reported (3) the identification of many alkylbenzenes and olefins in this fraction. In an extension of this work we now wish to report evidence for the presence of a series of C_{12} to C_{25} paraffins in cigar smoke condensate.

The presence of *n*- and iso-paraffins in tobacco leaf and in cigarette smoke has been investigated extensively by Carruthers and Johnstone (4) and by Kosak and Swinehart (5). More recently, Mold, *et al.* (6) have made a detailed study of the normal and branched chain paraffins (including anteiso branching) in the C_{25} to C_{33} range in cigarette tobacco. The presence of saturated hydrocarbons of low molecular weight in cigarette smoke has been reported by Patton and Touey (7) and other workers. Recently, Spears, *et al.* (8) have reported a quantitative study of the C_{12} to C_{33} alkanes in the smoke from burley, flue-cured, Turkish, and Maryland tobaccos. Similar reports have not appeared for the smoke from various cigar type tobaccos. Also, this is the first report, to our knowledge, of positive identification of the lower members of the smoke paraffins by other than gas chromatographic retention data.

Because of the wide range in molecular weights of compounds in this fraction, we decided to investigate the C_{12} to C_{25} range initially and have developed a technique for analysis of these compounds that is relatively fast, simple, and reproducible. Work is continuing on the isolation and identification of other paraffinic hydrocarbons not discussed in the present study.

METHOD

Conditions for smoking the cigars and trapping the smoke condensate have been described by Schepartz (9). A puff of 2 seconds' duration was taken every minute. The smoke was condensed in glass traps submerged in a CO_2-acetone bath. The isolation of the paraffinic hydrocarbons is outlined in Fig. 1. Fractionation of the smoke condensate to obtain nonpolar neutral substances in petroleum ether solution has been detailed in a previous publication (3). (In the present work, the order of precipitation by methanol and the 90% methanol extraction of the petroleum ether solution was arbitrarily reversed.) The residue (A) from the methanol codistillation was then taken up in an equal amount of water; this solution was extracted three times with petroleum ether (b.p. 60–70°C). The petroleum ether solution was dried over anhydrous magnesium sulfate for 24 hours. The dried solution was concentrated to 2 ml and chromatographed on a column (10 × 1″) of silicic acid (Mallinckrodt, activated at 110°C). Redistilled petroleum

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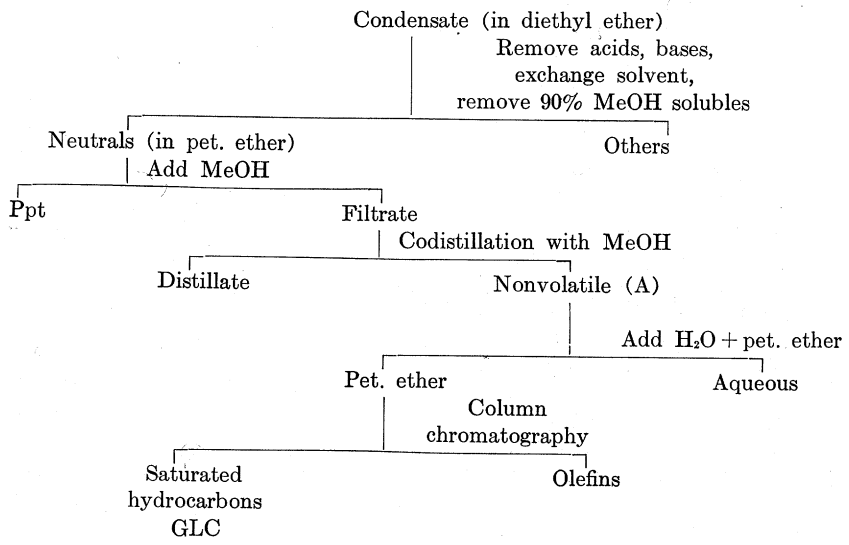

***Fig. 1*—Scheme for isolation of the paraffinic hydrocarbons.**

ether was used as the eluting solvent, and 15 ml fractions were collected. The fractions were analyzed for paraffinic hydrocarbons by gas-liquid chromatography (under conditions to be described) and checked for the presence of unsaturated components by ultraviolet spectral analysis and bromine uptake. The fifth and sixth fraction usually contained the paraffins in the C_{12} to C_{25} range; the sixth fraction also contained olefinic compounds. Fractions 5 and 6 were combined and rechromatographed on silicic acid to give paraffinic fractions (Fractions 5 and 6) free of olefinic contamination. This fraction was then concentrated *in vacuo* for gas chromatographic analysis on a Wilkins Aerograph Model A 350[4] (thermal conductivity detection). A 5 ft × 0.25″ column packed with SE-30 (0.25%) coated on glass beads (60–80 mesh) was used for the analysis under the following conditions: column temperature, 100 to 240°C at 8° per min.; carrier gas (helium) flow rate, 60 ml per min. (measured at 100°C); detector temperature, 260°C; and injector temperature, 260°C. Useful chromatograms were obtained by injecting an aliquot corresponding to four cigars.

The eluates corresponding to the peaks in the chromatogram were collected in U-shaped glass tubes (3 mm o.d.) submerged in a Dry Ice-acetone bath. The collected eluates were characterized by infrared spectra, mass spectra, and co-chromatography with known compounds. In most cases infrared spectra were taken on the neat liquid; however, the solid samples (C_{19} and above) were examined as KBr pellets. All spectra were obtained on a Perkin Elmer Model 237 Spectrophotometer. Mass spectra were obtained with the Model 21-103C Consolidated Electrodynamics Corporation instrument. The higher molecular weight compounds ($\geq C_{19}$) were introduced into the mass spectrometer by standard techniques for solid samples, and the other paraffins were introduced through a gallium frit by using a capillary. The inlet and source temperatures of the spectrometer were 250°C.

The amounts of the paraffins in the cigar smoke condensate were determined by gas chromatography. Area-concentration relationships were established for known paraffins of greater than 95% purity (as established by mass spectrometry). Losses in the isolation procedure were determined by dividing a sample of smoke condensate into two equal portions, adding known amounts of the paraffins to one of the portions, and determining the recoveries.

Solvent residues from the petroleum ether used in the isolation were checked for the paraffinic hydrocarbons found in cigar smoke. No hydrocarbons which could have contributed artifacts were found.

[4] Mention of a specific company or product does not constitute endorsement by the Department over other companies or products not mentioned.

Results and Discussion

The isolation procedure described in the experimental section was designed for relative ease of analysis and suitable recoveries. Previous workers in studying the paraffinic fraction of tobacco and cigarette smoke separated branched chain hydrocarbons from the normal isomers by the use of a molecular sieve. In one of these studies (6), the presence of anteiso (3-methyl) paraffins in addition to the known normal and iso compounds in the C_{25}–C_{33} range was demonstrated. We specifically fractionated the C_{25}–C_{33} compounds from the lower paraffins because of the difficulties they would present in trying to establish gas chromatographic conditions that would give a high degree of resolution. At the other extreme, a detailed analysis of the more volatile alkanes would require a totally different method of isolation (*see* ref. 6) than is applicable to the compounds in the C_{12} to C_{25} range. Under the chromatographic conditions described above for the compounds reported in this paper, the isoparaffins have retention times that differ from the retention times of both the normal-chain parent compounds and next lower normal-chain paraffin (the iso compounds have shorter retention times than the normal homologs in all cases). Confirmation of the absence of branched chain isomers in the chromatographic peaks was obtained by mass spectrometric analysis of collected eluates. Mold, *et al.* (6) have shown that selective fragmentation of branched-chain hydrocarbons occurs at the carbon bearing the side chain, thus giving a sensitive measure of contamination of normal with branched-chain isomers. Also, branched-chain isomers would elute with normal isomers of lower molecular weight and contribute to distinct mass spectral differences.

A typical chromatogram of the C_{12} to C_{25} paraffins is shown in Fig. 2. The degree of resolution depends, in part, on the age of the column. After approximately 10 chromatographic analyses, the column characteristics change so that the following peaks could not be resolved: 1 from 2, 3 from 4, and 5 from 6.

The compounds identified by gas chromatographic and mass spectral characteristics are as follows: peak 4, *n*-tridecane; peak 6, *n*-tetradecane; peak 8, *n*-pentadecane; peak 9, *n*-hexadecane; peak 11, *n*-heptadecane; peak 12, *n*-octadecane; peak 13, *n*-nonadecane; peak 14, *n*-eicosane; peak 15, *n*-heneicosane; peak 16, *n*-docosane; peak 17, *n*-tricosane; peak 18, *n*-tetracosane; and peak 19, *n*-pentacosane. Peak 21 appeared to be a mixture of C_{26}, C_{27}, and C_{28} paraffins. Because of the relatively small concentration and high volatility of the eluates corresponding to peaks 1, 2, 3, 5 and 10, their identities could not be fully confirmed. Tentatively, peak 1 has been identified as *n*-dodecane by gas chromatography. The mass spectrum of the eluate correspond-

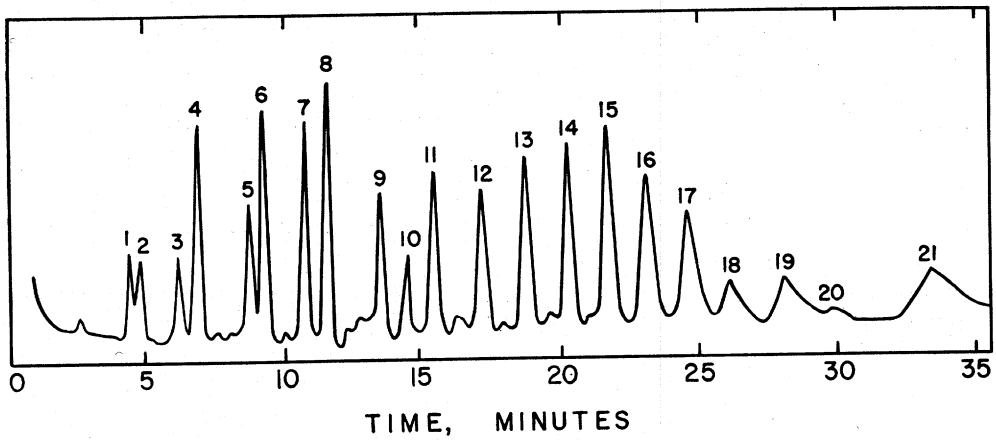

***Fig. 2*—Paraffins of cigar smoke condensate. See text for experimental details and peak identities.**

Table 1. Levels of C_{13}–C_{25} normal alkanes in cigar smoke condensate of four cigar types containing unblended filler

n-Alkane	Amount[a] (μg/cigar[b])			
	1[c]	2	3	4
Tridecane	4.8	6.0	5.6	4.5
Tetradecane	3.0	3.8	4.0	5.1
Pentadecane	3.2	8.3	7.0	8.0
Hexadecane	2.7	3.2	4.0	1.5
Heptadecane	1.7	3.3	5.4	2.5
Octadecane	1.5	3.4	5.5	3.0
Nonadecane	1.8	4.7	5.5	2.8
Eicosane	3.2	4.8	5.4	3.0
Heneicosane	2.8	5.7	5.6	3.2
Docosane	2.4	5.1	5.4	3.2
Tricosane	2.0	4.6	4.5	2.5
Tetracosane	1.0	2.0	—[d]	2.0
Pentacosane	1.2	1.7	—	—

[a] Amounts are uncorrected for recovery.
[b] Approximately 4 g of tobacco smoked per cigar (cigar length, about 13 cm, of which 8.6 cm was smoked).
[c] Figures represent average of two runs (25 cigars each) with a deviation of ± 10%.
[d] Areas could not be readily calculated.

ing to peak 7 is similar to that of a branched-chain C_{16} alkane (possibly 7-isopropyltridecane). The remaining small peaks located between those peaks corresponding to normal chain compounds are most likely branched-chain isomers. As Spears (8) has indicated, the amount of branched-chain isomers in the C_{12}–C_{25} range is many times smaller than the amount of the normal paraffins.

Levels of the paraffinic hydrocarbons in four cigars containing unblended fillers are summarized in Table 1. Control experiments indicate the unrecovered tridecane to be in the order of 60%; however, losses decrease rapidly (to 40% for tetradecane) and level off at eicosane (13% unrecovered). As indicated in Table 1, differences of about twofold and threefold are observed in some cases. The significance of these differences in the observed organoleptic differences among the cigars has not been established at this time.

Acknowledgments

The authors wish to thank Dr. R. L. Stedman for his assistance in the course of this work. They also wish to acknowledge the financial support of the project by the Cigar Manufacturers Association of America.

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